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PATENT SPECIFICATION

Inventor: ERIC BERTRAM EVANS

748,417

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COMPLETE SPECIFICATION

Improvements in or relating to methods of producing Metal Oxide Gels

We, ESSO RESEARCH AND ENGINEERING COMPANY, formerly known as Standard Oil Development Company, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the preparation of metal oxide-alumina gels such as are used for contact or catalytic purposes and more particularly it refers to a process for producing such compounds whereby aniline is reacted with aluminium and one or more other metals to form anilides, the said anilides being hydrolysed to form a hydrous metal oxide mixture, the aniline being regenerated and recycled.

According to the present invention there may be prepared mixed metal oxide gels such as aluminium-chromium oxide gel, aluminium-manganese oxide gel, aluminium-zinc oxide gel, aluminium-magnesium oxide gel, or aluminium-molybdenum oxide gel. To produce such gels the hydrous metal oxide which is obtained as a slurry may be dried and activated by well-known methods, or treated with impregnating solutions such as ammonium molybdate or chromic acid.

Petroleum naphtha and similar hydrocarbon mixtures containing appreciable quantities of naphthenes can be subjected to a reforming operation to yield a liquid product of improved octane number boiling within the gasoline range. Depending upon reaction conditions, catalytic reforming operations are generally referred to as either hydroforming or aromatization reactions. By hydroforming is ordinarily meant an operation conducted at elevated temperatures and pressures in the presence of a solid catalyst and added hydrogen wherein a hydrocarbon fraction is inrceased in aromaticity and wherein there is no net consumption of hydrogen. The term aromatization refers to an operation in which a hydrocarbon or hydrocarbon fraction is treated at elevated temperatures but at substantial atmospheric pressure in the presence of a solid catalyst for the purpose of increasing the aromaticity of the hydrocarbon or hydrocarbon fraction.

Catalytic reforming operations are usually carried out at temperatures of around 850g to 1100° F. in the presence of such catalysts as molybdenum oxide or chromium oxide supported on an alumina base or carrier.

In addition to the reforming processes, high boiling hydrocarbon materials may be converted to low boiling hydrocarbon materials by a process of catalytic cracking carried out by subjecting the high boiling hydrocarbon material to active conditions of temperature and pressure for sufficient time in the presence of catalysts such as alumina-magnesia, alumina-molybdena, alumina-silica-magnesia or alumina-silica-molybdena. The catalyst may be in the form of fixed or moving bed with the vaporized high boiling hydrocarbon material passing therethrough or the so-called fluid technique may be used in which the catalyst material is suspended in vapours or high boiling hydrocarbon maerial during the recation. Other catalytic conversions of hydrocarbons or other compounds may be practised using the catalysts prepared according to the present process.

Our British Patent Specification No. 719,723 described a process for the preparation of alumina-containing mixed metal oxide gels used as catalysts in hydrocarbon operations described above, whereby aluminium alloys are reacted with phenols or cresols, the said phenates or cresylates being subsequently hydrolysed with the formation of mixed hydrous metal oxides, the phenol or cresol being subsequently regenerated. It is necessary in processes of this type that the regenerated compounds are freed from water before being recycled, and an advantage in the use of the pre-

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sent invention that the solubility of aniline in water is much less than that of phenol, and is of the same order as the solubility of cresols, is shown in Table I. This property allows much better separation of regenerated aniline and compounds, and allows greater efficiency of reaction.

TABLE I

	Solubility in water—gms/100 mls.H_2O	
Aniline	3.4 at 20° C.	6.4 at 90° C.
Phenol	6.7 at 16° C.	00 at 66° C.
o-cresol	3.1 at 40° C.	5.6 at 100° C.
m-cresol	2.4 at 20° C.	5.8 at 100° C.
p-cresol	2.4 at 40° C.	5.3 at 100° C.

The present invention, besides using the sparingly soluble aniline, produces products of high purity and surface area.

The preparation of metal gels may be carried out by adding the metal in any suitable form such as turnings, powder, granules or chips, to the anhydrous aniline. A reaction catalyst may also be added; suitable catalysts being mercuric chloride or other mercury salts, the amount of such reaction catalysts being preferably from 0.01 to 1% by weight based on the metal employed.

The reaction mixture should be heated to the boiling point of the aniline to initiate reaction, and this temperature maintained during the progress of the reaction.

Hydrogen produced during the reaction may be removed overhead. The reaction should preferably be carried out under reflux.

The products of reaction comprising mixed metal anilides may be hydrolysed in the reaction zone or may be passed to a suitable hydrolysis zone which may be an orifice mixer or a centrifugal pump. Hydrolysis may be carried out with water, steam or an aqueous colloidal solution such as silica, hydrosol or silica hydrogel, or an impregnating aqueous solution to hydrolyse the anilide solution forming the hydrous alumina metal oxide complex salt. The temperature during hydrolysis may be between 212° F. and 400° F.

During hydrolysis with silica hydrosol or silica hydrogel, water is removed from the hydrosol or hydrogel to form the silica-alumina metal oxide composite which can be dried. When using an impregnating solution such a solution of a metal salt such as ammonium molybdate or chromic acid, the solution may be added to the slurry of alumina metal oxide complex obtained from the hydrolysis reaction, and the sulplus removed and the product gently dried to obtain the desired complex.

The invention therefore comprises an improved process for producing alumina-containing mixed metal oxides gels, which comprises reacting aluminium and one or more other metals or metal alloys with anhydrous aniline at an elevated temperature, and hydrolysing the metal anilides thereby obtained to form a hydrous mixed metal oxide complex and drying the said hydrous mixed metal oxide coupler to form an adsorbent mixed metal oxide gel.

The invention may be further understood by reference to the following example.

EXAMPLE

A mixture of pure powdered aluminium and magnesium in equal proportions was treated with an excess of pure aniline in a three-necked flask together with 0.5% by weight of mercuric chloride as a reaction catalyst. The reaction mixture was heated to boiling point under reflux and continually stirred at that temperature for about 3 hours. On cooling, the contents of the flask were poured into a container and a quantity of distilled water added. Aniline was immediately liberated, together with a gel-like formation of a mixture of aluminium and magnesium hydroxide. The surplus water was removed from the gel by treatment with anhydrous alcohol, followed by ether extraction, and the resulting gel gently dried.

Similar results were obtained using aluminium and manganese, using the reaction conditions described above.

What we claim is:—

1. An improved process for producing alumina-containing mixed metal oxide gels, which comprises reacting aluminium and one or more other metals or alloys with anhydrous aniline at an elevated temperature, and hydrolysing the anilides thereby obtained to form a hydrous mixed metal oxide complex, and drying the said hydrous mixed metal oxide complex to form an adsorbent mixed metal oxide gel.

2. A process as claimed in Claim 1 wherein the said other metal reacted with the said aniline is molybdenum, manganese or magnesium.

3. A process as claimed in Claim 1 or Claim 2 wherein an impregnation solution of ammonium molybdate or chromic acid is added to the said mixed hydrous metal oxide before drying.

4. A process as claimed in any of Claims 1 to 3 wherein 0.01 to 1% by weight based on the metal employed of a mercury salt, preferably mercuric chloride, is added to the anhydrous aniline as a reaction catalyst.

5. A process as claimed in any of Claims 1 to 4 wherein the metal anilide is hydrolysed with silica hydrosol or silica hydrogel, whereby a mixed metal oxide gel-silica composite is obtained.

K. J. VERYARD,
33, Davies Street, London, W.1,
Agent for the Applicant.

PROVISIONAL SPECIFICATION

Improvements in or relating to methods of producing Metal Oxide Gels

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare this invention to be described in the following statement:—

This invention relates to a process for the preparation of metal oxide gels such as are used for contact or catalytic purposes and more particularly it refers to a process for producing such compounds whereby aniline or a mono-N-alkyl substituted aniline is reacted with a metal or alloy to form anilides, the said anilides being hydrolysed to form a hydrous metal oxide, the aniline compound being regenerated and recycled.

According to the present invention there may be prepared metal oxide gels such as alumina gel, zinc oxide gel, chromium oxide gel, manganese gel, or compound metal gels such as zinc-aluminium gel, aluminium magnesium gel, aluminium-chromium gel, aluminium-manganese gel, or aluminium-molybdenum gel. To produce such gels the hydrous metal oxide which is obtained as a slurry may be dried and activated by well-known methods, or treated with impregnating solutions such as ammonium, molybdate, or chromic acid.

Petroleum naphtha and similar hydrocarbon mixtures containing appreciable quantities of naphthenes can be subjected to a reforming operation to yield a liquid product of improved octane number boiling within the gasoline range. Depending upon reaction conditions, catalytic reforming operations are generally referred to as either hydroforming or aromatization reactions. By hydroforming is ordinarily meant an operation conducted at elevated temperatures and pressures in the presence of a solid catalyst and added hydrogen wherein in a hydrocarbon fraction is increased in aromaticity and wherein there is no net consumption of hydrogen. The term aromatization refers to an operation in which a hydrocarbon or hydrocarbon fraction is treated at elevated temperatures but at substantial atmospheric pressure in the presence of a solid catalyst for the purpose of increasing the aromaticity of the hydrocarbon or hydrocarbon fraction.

Catalytic reforming operations are usually carried out at temperatures of around 850° to 1100° F. in the presence of such catalysts as molybdenum oxide, chromium oxide and the like. These catalysts are usually supported on a base or carrier, the most commonly used base being alumina. In this invention, alumina based catalysts consisting of one or more of the Group VI oxides such as molybdenum oxide or chromium oxide, supported on alumina have been prepared and used as reforming catalysts.

In addition to the reforming processes, high boiling hydrocarbon materials may be converted to low boiling hydrocarbon materials by a process of catalytic cracking carried out by subjecting the high boiling hydrocarbon material to active conditions of temperature and pressure for sufficient time in the presence of catalysts such as alumina, alumina-boria alumina-silica alumina-silica-magnesia alumina-magnesia and the like. The catalyst may be in the form of fixed or moving bed with the vaporized high boiling hydrocarbon material passing therethrough or the so-called fluid technique may be used in which the catalyst material is suspended in vapours or high boiling hydrocarbon material during the reaction. Other catalytic conversions of hydrocarbons or other compounds may be practised using the catalysts prepared according to the present process.

Our copending Application No. 6530/52 described a process for the preparation of metal oxide gels used as catalysts in hydrocarbon operations described above whereby metals are reacted with phenols or cresols the said phenates or cresylates being subsequently hydrolysed with the formation of hydrous metal oxides the phenol or cresols being subsequently regenerated. It is necessary in processes of this type that the regenerated compounds are freed from water before being recycled and an advantage in the use of the present invention that the solubility of aniline or N-acyl substituted compounds in water is much less than that of phenol and is of the same order as the solubility of cresols is shown in Table I. This property allows much better separation of regenerated aniline and compounds and allows greater efficiency of reaction.

TABLE I

	Solubility in water—gms/100 mls.H_2O	
Aniline	3.4 at 20° C.	6.4 at 90° C.
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m-cresol	2.4 at 20° C.	5.8 at 100° C.
p-cresol	2.4 at 40° C.	5.3 at 100° C.

The present invention besides using the sparingly soluble aniline compounds produces products of high purity and surface area.

The preparation of metal gels may be carried out by adding the metal in any suitable form such as turnings powder granules or chips to the anhydrous aniline compound. A reaction catalyst may also be added. Suitable catalysts being mercuric chloride or other mer-

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cury salts the amount of such reaction catalysts being preferably from 0.01 to 1% by weight based on the metal.

The reaction mixture should be heated to the boiling point of the aniline or substituted compound to initiate reaction and this temperature maintained during the progress of the reaction. Using aluminium and aniline for the production of alumina gel the reaction may be represented by the following equation:—

$$6C_6H_5NH_2+2Al=2Al(NHC_6H_5)_3+3H_2$$

The hydrogen may be removed overhead. The reaction should preferably be carried out under reflux.

The products of reaction comprising a solution of metal anilide may be hydrolysed in the reaction zone or may be passed to a suitable hydrolysis zone which may be an orifice mixer or a centrifugal pump. Hydrolysis may be carried out with water steam or an aqueous colloidal solution such as silica hydrosol or silica hydrogel or an impregnating aqueous solution to hydrolyse the anilide solution forming the hydrous metal salt. The temperature during hydrolysis may be between 35° F. and 400° F. The reaction at this stage may be represented by the following equation again using the aluminium compound for the purpose of illustration:—

$$2(C_6H_5NH)_3Al+6H_2O= Al_2(OH)_6+6C_6H_5NH_2$$

During hydrolysis with silica hydrosol or hydrogel, water is removed from the hydrosol or hydrogel to form the silica-metal oxide composite which can be dried. When using an impregnating solution such as a solution of a metal salt such as ammonium molybdate or chromic acid solution is added to the slurry of metal oxide obtained from the hydrolysis reaction and the product dried to obtain the desired complex. Alternatively complexes may be obtained by reacting the aniline compound with alloys such as aluminium-zinc aluminium-manganese or aluminium-magnesium.

The invention therefore comprises an improved method for producing metal oxide gels, which comprises reacting a metal or a metal alloy with anhydrous aniline or a mono-N-alkyl substituted aniline, preferably methyl aniline, at an elevated temperature and hydrolysing the metal anilide obtained therefrom to form a hydrous metal oxide or metal oxide complex and drying the said hydrous metal oxide or metal oxide complex to form an adsorbent metal oxide complex.

K. J. VERYARD,
Brettenham House, (Sixth Floor South),
Lancaster Place, London, W.C.2,
Agent for the Applicant.

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